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GB 1233952

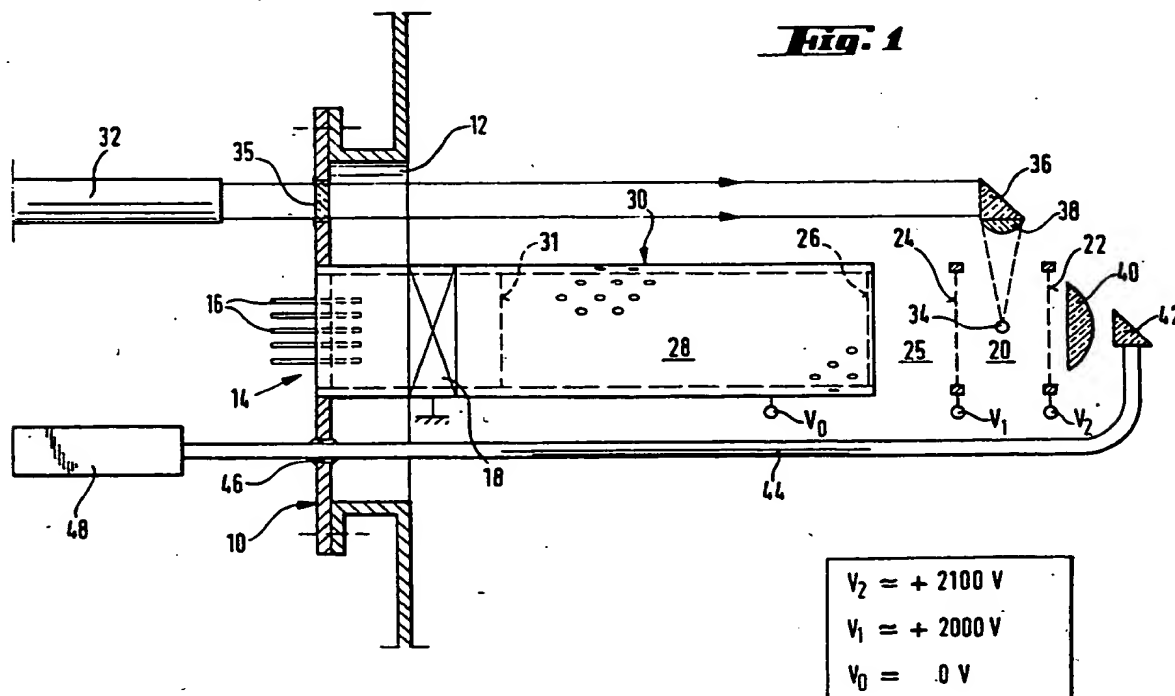
(58) Field of search

H1D

Selected US specifications from IPC sub-class H01J

(54) Mass spectrometer

(57) A laser mass spectrometer comprises an electrode system and an ion detector system 18 supported on a mounting flange 10 through which their electrical connections 16 pass. The electrode system defines an ionisation space 20, an ion acceleration space 25 and a time-of-flight path 28 which is surrounded by a shield electrode 30. The shield electrode 30 and the electrode system are removably mounted on support rods (66) extending in the axial or ion path direction, to allow accommodation to an adjacent apparatus or vacuum system. The distance between the mounting flange 10 and the ionisation space 20 may be varied to provide time-of-flight paths of different length. Ionisation is effected by radiation from a laser 32 which passes through a window 35 in the flange. A light guide is also provided for directing radiation emitted by an ionized substance in the space 20 to spectroscopic apparatus 48.



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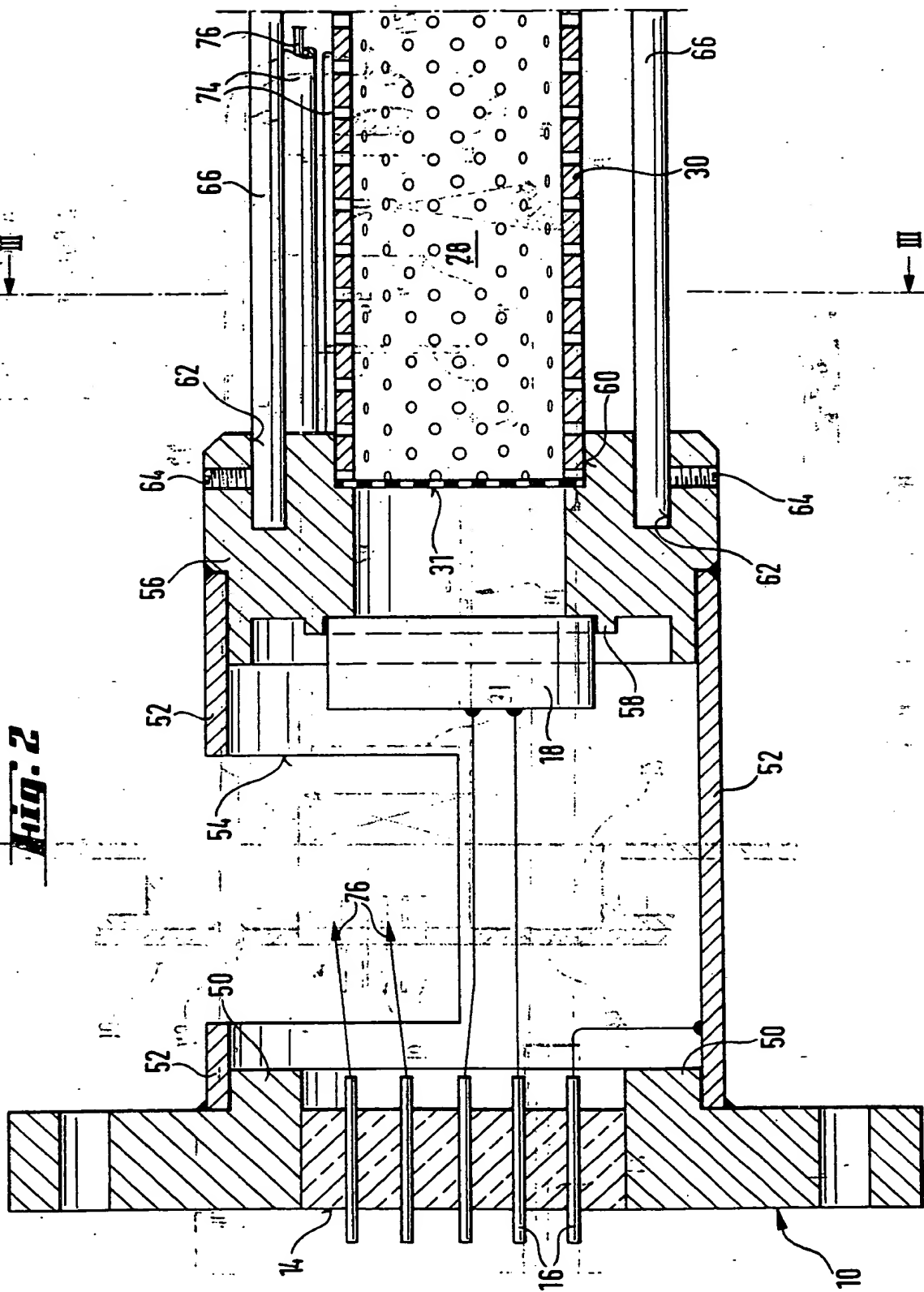


Fig. 3

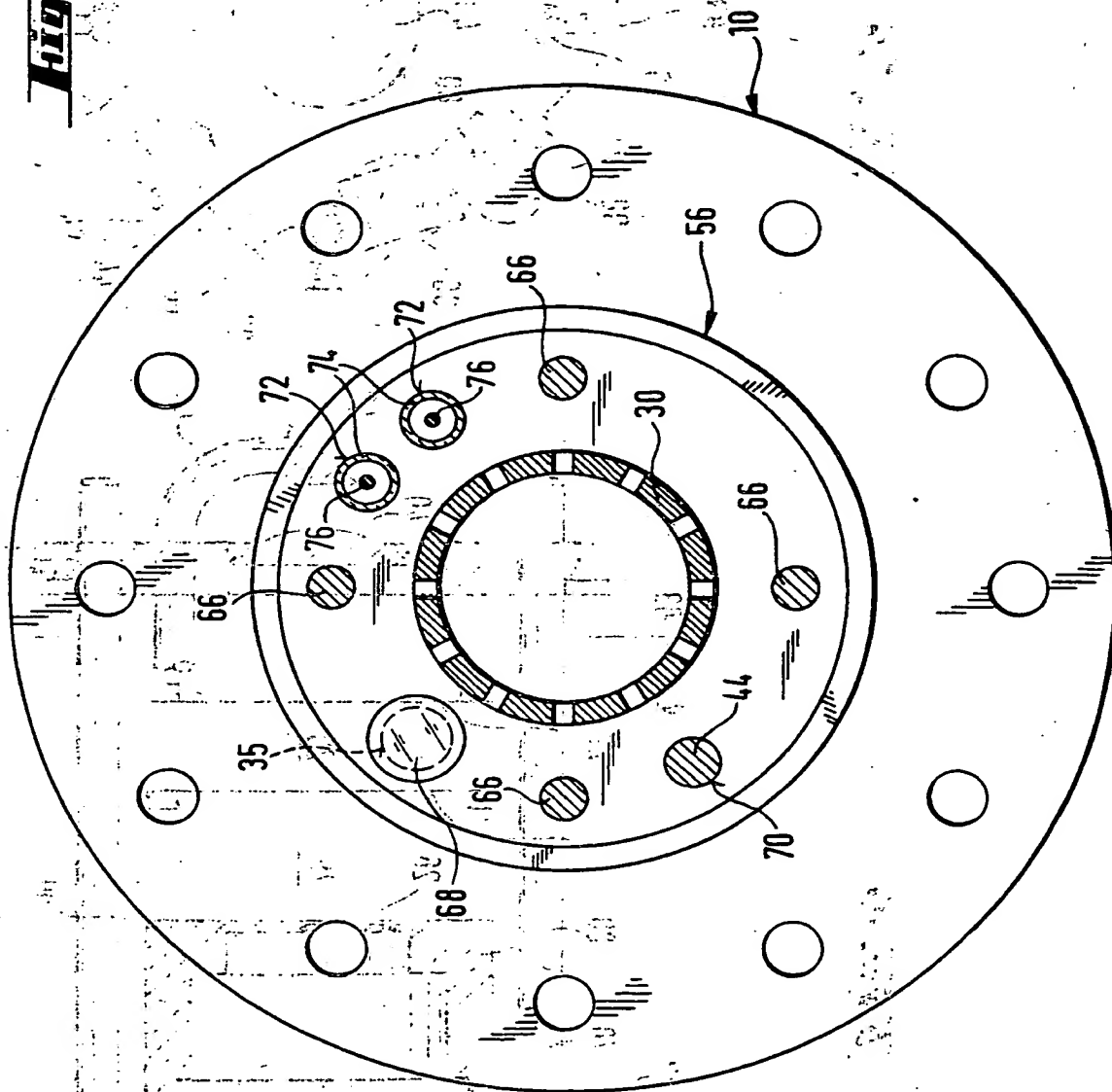


Fig. 5

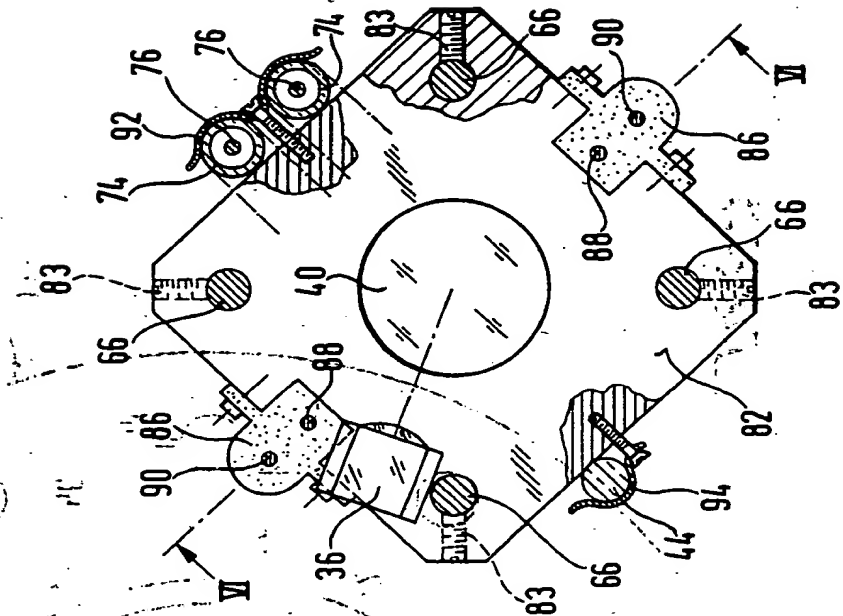


Fig. 4

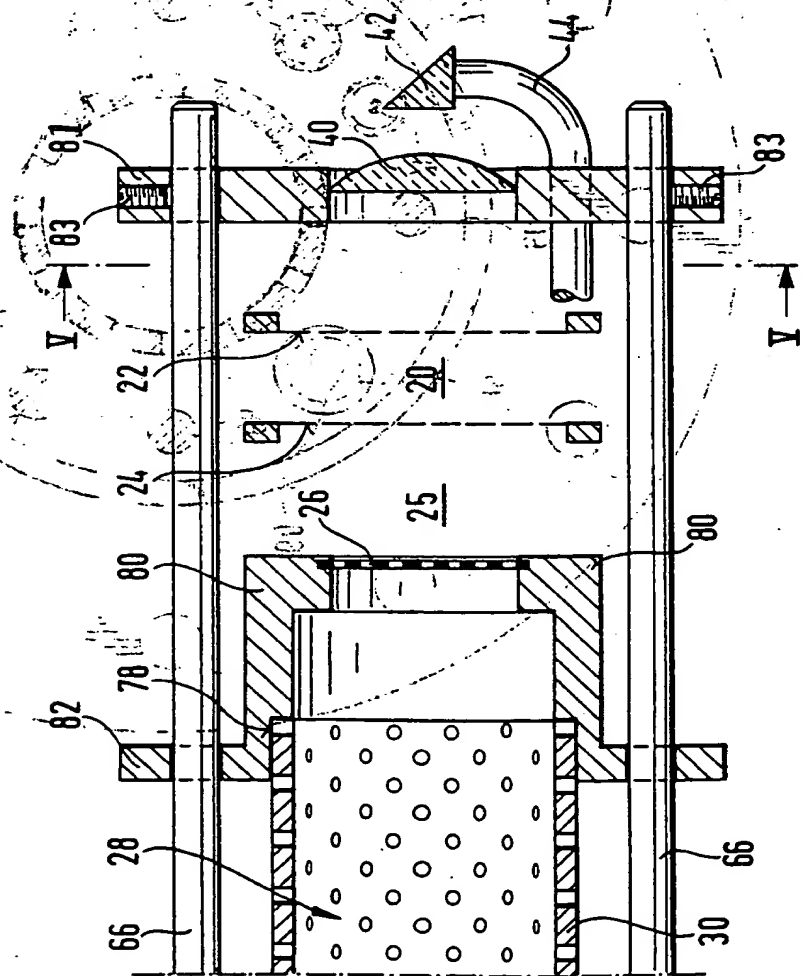
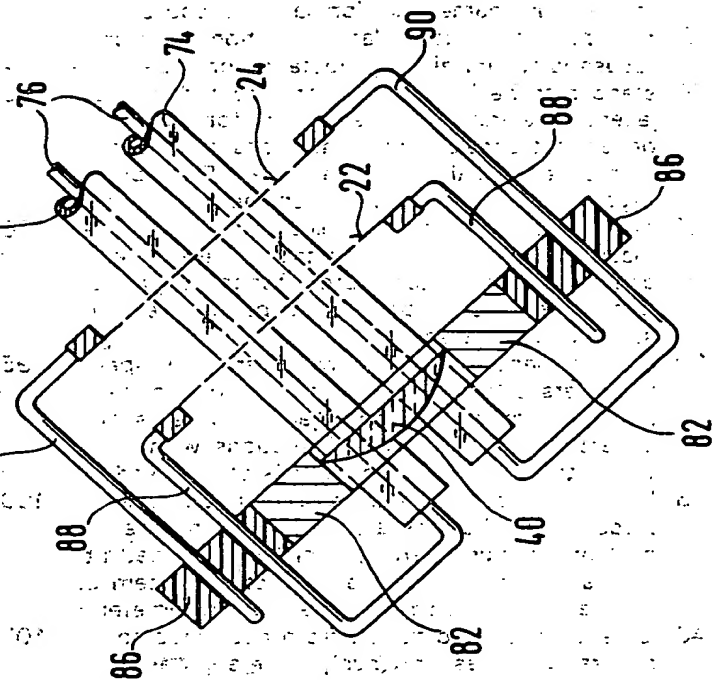


Fig. 6



SPECIFICATION

Mass spectrometer

5 The present invention relates to a mass spectrometer, more specifically a mass spectrometer in which a substance to be investigated is ionized by laser radiation.

A mass laser spectrometer of this general type is described in the applicants publication "Ultrasensitive Fingerprint Detection of Organometallic Compounds by laser Multiphoton Ionisation Mass Spectrometry" Appl. Phys. Lett. 45 (11), 1 December 1984.

15 Mass spectrometers of this type generally comprise, as main components, along an axis in the order named: an ionisation space or chamber into which a laser radiation beam is focussed for ionizing a substance or substances to be investigated or detected; an adjacent acceleration space or path for mass-dependent acceleration of the ions produced, then an essentially fieldfree time-of-flight or separation space, within which the ions with different e/m ratios (e = electric charge; m = mass), separate because of their different velocities, and a detector system for the separated ions. The ionisation may be wavelength selective or insensitive.

30 A deficiency of the known laser mass spectrometers of this type is that they cannot be accommodated easily to adjacent systems or apparatus of different configurations with which the mass spectrometer is to be used.

35 More specifically, the distance between the place where the ions are produced and the port or mounting flange, (which is provided at the vacuum vessel of the respective system or apparatus with which the mass spectrometer is used) is quite different from apparatus to apparatus. It has previously generally been necessary to modify the apparatus to align it with an existing commercial mass spectrometer.

45 A further problem encountered with the known mass spectrometers is that molecular substances are often severely fragmented by the ionizing radiation so that ions of parts of the original substance, rather than the so-called "parent" (or "mother") ion, are produced and detected.

It is further desirable to obtain further information about the substance under investigation in addition to that provided by the mass spectrogram.

55 The present invention attempts to solve or alleviate these problems. According to a first aspect a mass spectrometer comprises an electrode system having a plurality of control electrodes, defining an ionisation space and an ion accelerating space; a shield electrode surrounding a time-of-flight separation path; the ionisation space, the acceleration space and the separation path being arranged in the order named along an axis; detector means positioned at the end of the separation path remote from the acceleration space; a mounting flange provided with means for electrical connection of the control electrode and of the ion detector means; and the shield electrode being removably mounted on support members extending in the said axial direction.

70 The means for electrical connection preferably comprises connecting means passing through the mounting flange (lead-through means).

According to a second aspect a mass spectrometer comprises an electrode system defining an ionisation space, an ion acceleration space, separation means and detector means positioned in the order named along an axis, means for ionizing a substance within the ionisation space, and means for coupling out radiation emitted in the ionisation space.

85 In a preferred embodiment of the present invention, the electrode encompassing the separation path is mounted on axially extending support members so that it can be easily replaced by a similar electrode of different length. At least one of a pair of electrodes defining the ionization space may be mounted on electrical conductors which in turn are mounted axially adjustably on mounting members supported by a removable support body.

90 The invention may be carried into practice in various ways and one specific embodiment will now be described by way of example, with reference to the drawings, in which: Figure 1 is a simplified view of a laser mass spectrometer in accordance with the present invention;

100 Figure 2 is an axial section of a flange end of a preferred embodiment of a laser mass spectrometer;

105 Figure 3 is a view in the direction of the arrows III-III of Figure 2;

Figure 4 is an axial section of the ion source end of the mass spectrometer of Figure 2;

Figure 5 is a view in the direction of the arrows 5-5 of Figure 4, and

Figure 6 is a section along the line VI-VI of Figure 5.

As shown schematically in Figure 1, a mass spectrometer comprises a measuring system with a coupling flange 10 which allows one to mount the measuring system in an air-tight manner on a flanged port 12 of a vacuum system (not shown) in which a substance to be investigated by mass spectrometry is present or generated. It is a feature of the present embodiment that all parts of the measuring system are supported by the flange 10. Thus, the measuring system protrudes in a cantilever fashion from the flange into the inner of the vacuum system. The flange 10 comprises electrical lead-in means 14 (similar to an electron tube stem) having a plurality of terminal pins 16. An ion detector system 18 is mounted adjacent the flange, said system comprising preferably a double channel-plate

multiplier, i.e. a plate system having a multitude of small diameter channels operating as secondary electron multipliers. Such ion detectors are known and various types thereof are commercially available; no further explanation is therefore considered necessary. In operation, a conventional electronic control and signal processing apparatus (not shown) is connected to the terminals 16 of the measuring system.

An ionisation chamber or space 20 defined by a pair of parallel, plane grid or mesh electrodes 22, 24 having annular support rings is provided at the end of the measuring system remote from the mounting flange. A further grid or mesh electrode 26, which together with the electrode 24 defines an ion acceleration space 25, is provided on the detector side of the electrode 24 in spaced relationship therefrom. An essentially field-free separation or time-of-flight path 28 is provided between the electrode 26 and the ion detector 18. The path 28 is enclosed and shielded by a cylindrical electrode 30 made of thin perforated sheet metal and has a grid or mesh electrode 31 at the end facing the flange 10. The electrodes 26 and 31 are electrically connected to the cylindrical electrode 30, so that the path 28 is substantially free of electrical fields.

A laser 32 is provided for producing a radiation beam which is focussed into a focus region 34 within the ionisation space. The laser may be a dye laser, a frequency doubled dye laser or an excimer laser. Preferably, a synchronously pumped dye laser in combination with an excimer laser amplifier pumped by an argon laser is used, e.g. a dye laser of the type Coherent 599, a Lambda Physics type EMG 103 excimer laser, and an argon pump laser type CR18 are used to produce a radiation beam having a wave-length of 590 nanometers or, if frequency doubling is used, a wave length of 295 nanometers. Lasers of this type are adapted to produce radiation pulses having a duration down to few picoseconds. This allows one to detect also relatively unstable molecules, such as metalloorganic compounds and the like, without fragmentation (breaking up). While the laser radiation may be coupled into the vacuum system and the ionisation space in a direction normal to the longitudinal axis of the mass spectrometer system through a window provided in the wall of the vacuum system with which the mass spectrometer is used, the preferred embodiment has an entrance window 35 in the mounting flange. The laser beam travels first essentially parallel to the longitudinal axis of the mass spectrometer, and then through the window to a prism 36 or another reflector which is provided on the side of the ionisation space 20 and which deflects the beam by 90°. The deflected beam is focussed by a lens 38 (which may be integrally formed with the prism 36) into the fo-

cus region 34 within the ionisation space 20. Alternatively, a light guide system as a light conducting fibre or rod or fibre-bundle may be used for directing the laser radiation into the vacuum system and the ionisation space.

The ions generated within the focus region 34 are transferred into the acceleration space 25 by a weak drift field typically of 100 volts between the electrodes 22 and 24, and then accelerated by an accelerating voltage of typically about 2000 volts between the electrodes 24 and 26. Since the acceleration of a charged particle by an electric field depends on the mass of the particle, more specifically on the ratio of e/m , as is well known, the ions enter the separation path 28 through the grid electrode 26 with velocities which are inversely proportional to the square root of the ratio of their charge e to their mass m . Ions with differing values of e/m separate due to their differing velocities along the path 28 and arrive therefore at the ion detector at differing times after the radiation pulse by which they are generated. The principle of such time-of-flight mass spectrometers is well known in the art; no further explanation is therefore considered necessary.

Not only the ions produced in the focus region 34 are used for analysing the substances which are present in the ionization space, but also used is the optical radiation (especially fluorescence radiation) emitted by the respective substances within the ionisation space. Thus, two different types of information can be simultaneously derived from a single laser radiation pulse ("shot"), i.e. mass spectrum information and optical-spectroscopic information. For this purpose, the optical radiation emitted from the excited substances within the focus region 34 may be focussed by a lens 40 (which may be a Fresnel lens) via a prism 42 into a light guide 44 (e.g. a fibre bundle or monofilament light guide), which is lead out at 46 in an air-tight manner through the flange 10 to the outside of the vacuum space. The radiation is then passed to a spectroscopic apparatus 48 which separates the radiation on the basis of the wave-length by a diffraction grating or prism in a well known manner.

A preferred configuration of the mass spectrometer shown in Figure 1 will now be described with reference to Figures 2 to 6. The same components are provided with the same reference numerals as in Figure 1.

The vacuum or inner side of the flange 10 is provided with an annular boss 50, on which a metal tube is mounted. The metal tube has a cut-out 54 on its one side. An annular body 56 is mounted on the end of the metal tube 52 remote from the flange 10. The surface of the body 56 facing the flange 10 forms a seat means 58 for the ion detector 18. The seat means has an annular rib to accommodate ion detectors of different commercially available

- types. A seat 60 is formed on the side of the body 56 which is remote from the flange 10. The seat 60 receives the electrode 31 and supports one end of a perforated sheet metal tube which forms the electrode 30. Further, four holes are provided on this side, each receiving a support rod 66. Each support rod 66 is fixed in the respective hole 62 by a screw 64 which is shown only schematically.
- As shown in Figure 3, the body 56 has a window 68 through which the laser beam is projected and which is aligned with the window 35 (Figure 1). Further, the body 56 has an aperture 70 for the light guide 44 (Figure 1) and apertures 72 for electrical conductors 76 (Figure 6) connecting to the electrodes 22 and 24. The conductors 76 are insulated by glass tubes 74, as best seen in Figures 5 and 6.
- As shown in Figure 4, the electrode 30, which surrounds the separation path 28, is seated with its end remote from the ion detector 18 in an annular recess 78 of a generally tube-shaped metal body 80, which is supported by an integral flange 82 on the rods 66. The flange 82 can be used for separating the vacuum space defined by a tubular part (not shown) of the envelope of the vacuum system surrounding the electrode system described and has apertures (not shown) for the conductors 76, the laser beam and the light guide 44. The opening of the metal body 80 which is remote from the separation path 28 is provided with the grid or mesh electrode 26.
- All grid or mesh electrodes are preferably made of thin perforated nickel metal foils; their open area is as large as possible and may in practice be 80% or more.
- An essentially square plate 81 of stainless steel is seated on the rods 66 near their ends. The rods traverse corresponding holes near the corners of the plate 81 and are fixed with respect to the plate by set screws 83. The plate has a center hole in which the lens 40 is seated. Insulating support members 86 are attached by screws on opposed edges of the plate 81. Each of the support members has two apertures for receiving bent support wires 88 and 90, respectively (Figure 6) which are each connected to the corresponding conductor 76 and provide for mechanical support and electrical connection of the electrodes 22 and 24, respectively.
- As shown in Figure 5 the glass tubes 74 which insulate the conductors 76 are held to one side of the edge of the plate 81 by a spring clamp 92. A further spring clamp 94 is provided on the opposite side of the edge of the plate 92 for positioning the light guide 44. The prism 36 is supported on the plate 82 by appropriate uprights.
- The above described embodiment of the mass spectrometer measuring system may have an outer diameter of about 63 cm, so that it fits easily through a mounting flange of a usual vacuum system. The system can be easily adapted to different situations. It has been found that the length of the separation path 28 is not very critical and may vary between 20 cm and 100 cm or more without impairing the resolution of the time-of-flight mass spectrometer beyond a limit which is acceptable for many applications. Thus, the distance between the ionisation space 20 and the mounting flange 10 can be easily adjusted by cutting the perforated sheet metal forming the electrode 30 to the desired length. The other components, such as the rods 66, the glass tubes 74 and so on, the lengths of which may also have to be adjusted to the desired distance between the ionisation space 20 and the mounting flange 10, can also be easily trimmed to the required length.
- The electrodes 22, 24, 26 and 30 of the above described preferred embodiment of the invention are made of nickel. The laser 32 of the preferred embodiment is a synchronously pumped dye laser type Coherent 599 followed by an excimer laser amplifier type Lambda Physics EMG 103, pumped with an argon laser type Coherent CR 18. The laser system 32 produces radiation pulses having a wavelength of about 590 nanometer (or if desired, after frequency doubling, a wavelength of about 295 nanometers) and an energy of the order of microjoules to millijoules per pulse. The pulse length is about 10 picoseconds and may be even shorter (e.g. 2 picoseconds or less) to prevent undue fragmentation of molecular substances to be analyzed and to allow the detection of the so-called parent (or mother) ion. A pulse length of about 10 picoseconds has been found to be an acceptable compromise between costs and the detection sensitivity of the parent ion, since lasers for producing pulses with lengths in the order of few picoseconds are still rather expensive. If the detection of the parent ion is of lesser concern, pulse lengths up to e.g. 20 nanoseconds may be used; if the costs are of no concern, pulse lengths of 2 picoseconds or less are preferred.
- Various modifications of the disclosed embodiment will occur to those skilled in the art without departing from the scope of the invention as defined by the appended claims. Thus, the electrode 22 may be affixed to and supported by the plate 82. Tube support members may be used instead of the relatively thin solid rods 66 and the conductors for connecting the electrodes may extend through these tubes which may consist of an insulating material, such as ceramic. The electrodes 22 and 24 may be attached to the ends of an insulating tube or may each be mounted on an individual stainless steel plate corresponding to the plate 82; in this case the mounting wires 88 and 90 may be offset by 90 degrees or mounted on individual support

members 86 mounted on different sides of the respective plates.

CLAIMS

- 5 1. A mass spectrometer comprising an electrode system having a plurality of control electrodes (22, 24, 26, 30), defining an ionisation space (20) and an ion accelerating space (25); a shield electrode (30) surrounding a time-of-flight separation path (28); the ionisation space (20), the acceleration space (25) and the separation path (28) being arranged in the order named along an axis; detector means (18) positioned at the end of the separation path (28) remote from the acceleration space (25); a mounting flange (10) provided with means (16) for electrical connection of the control electrodes and of the ion detector means; and the shield electrode (30) being removably mounted on support members (66) extending in the said axial direction.
- 10 2. A mass spectrometer as claimed in Claim 1 in which all of the control electrodes, and the detecting means, are supported in a cantilever fashion from the mounting flange (10).
- 15 3. A mass spectrometer as claimed in Claim 1 or Claim 2 in which the ionisation space (20) is provided at the end of the separation path (28) remote from the mounting flange (10).
- 20 4. A mass spectrometer as claimed in any one of Claims 1 to 3 in which the shield electrode (30) has a tubular shape and is supported with its ends in seat means (60, 78) formed by annular members (56, 80), at least one (80) of the annular members being removably mounted on the support members (66).
- 25 5. A mass spectrometer as claimed in any one of the preceding claims in which the ionisation space (20) is defined by a pair of the control electrodes, at least one of the control electrodes of the said pair being mounted on electrical conductors (88, 90) which in turn are mounted on a removable mounting member (82) supported by the support members (66).
- 30 6. A mass spectrometer as claimed in any one of the preceding claims in which the ends of the support members (66) facing the mounting flange (10) are removably mounted on an annular end-support (56), the annular end-support being mounted on the support flange (10) by means of a tubular member (52) having a lateral aperture (54).
- 35 7. A mass spectrometer as claimed in Claim 6 in which the annular end-support (56) also forms seat means (58) for the ion detecting means (18).
- 40 8. A mass spectrometer as claimed in any one of the preceding claims in which the support members (66) are axially extending rod-shaped members.
- 45 9. A mass spectrometer as claimed in any one of Claims 1 to 7 in which the support members (66) are axially extending tubes.
- 50 10. A mass spectrometer as claimed in any one of the preceding claims in which means are provided for allowing an ionizing radiation to enter the ionisation space (20) through the mounting flange (10).
- 55 11. A mass spectrometer as claimed in any one of the preceding claims having means (40, 42, 44) for coupling radiation out of the ionisation space (20).
- 60 12. A mass spectrometer as claimed in Claim 11 including means for analysing the coupled-out radiation.
- 65 13. A mass spectrometer as claimed in Claim 11 or Claim 12 in which the coupling-out means (40, 42, 44) is adapted to guide the radiation through the mounting flange (10).
- 70 14. A mass spectrometer as claimed in any one of the preceding claims in which the distance between the mounting flange (10) and the ionization space (20) is adjustable.
- 75 15. A mass spectrometer as claimed in any one of the preceding claims including laser means for producing a laser beam directed into the ionisation space, the laser means being adapted to produce radiation pulses of a duration of no more than about 10 picoseconds.
- 80 16. A mass spectrometer as claimed in any one of the preceding claims in which the shield electrode is of perforated sheet metal.
- 85 17. A mass spectrometer comprising an electrode system defining an ionisation space, an ion acceleration space, separation means and detector means positioned in the order named along an axis, means for ionizing a substance within the ionisation space, and means for coupling out radiation emitted in the ionisation space.
- 90 18. A mass spectrometer as claimed in Claim 17 including means for analysing the coupled-out radiation.
- 95 19. A mass spectrometer as claimed in Claim 17 or Claim 18 in which the means for ionizing the substance comprises a laser (32).
- 100 20. A mass spectrometer as claimed in Claim 17 in which the laser is adapted to produce radiation pulses of no more than about 10 picoseconds in length.
- 105 21. A mass spectrometer substantially as specifically herein described with reference to the drawings.